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COMMUNICATIONS

Rotational motion compensates the energy defect in near-resonant vibration–vibration energy transfer: A state-to-state study of $\text{NO}(v) + \text{N}_2\text{O}$ Marcel Drabbels^{a)} and Alec M. Wodtke*Department of Chemistry, University of California, Santa Barbara, California 93106*

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Our lack of understanding of the factors that compensate energy defects in near resonant V–V energy transfer constrains our ability to accurately predict resonance widths and, thus, the overall importance of such processes. We have carried out one of the first truly state-to-state measurements of near resonant V–V energy transfer under single collision conditions, employing the crossed molecular beams, stimulated emission pumping technique. We have varied the energy defect ΔE for the process: $\text{NO } X^2\Pi(v) + \text{N}_2\text{O}(0,0,0) \rightarrow \text{NO } X^2\Pi(v-1) + \text{N}_2\text{O}(0,0,1)$, by changing the prepared vibrational state from $v=22$ ($\Delta E = +14 \text{ cm}^{-1}$) to $v=21$ ($\Delta E = -18 \text{ cm}^{-1}$) to $v=20$ ($\Delta E = -49 \text{ cm}^{-1}$). Changes in the energy transfer efficiencies and rotational distributions of vibrationally inelastically scattered NO with energy defect both strongly suggest that molecular rotation (both of NO and N_2O) is responsible for compensating the energy defect. Furthermore it appears that relative translation is ineffective in compensating the energy defect. A $\Delta J_{\text{NO}} \sim \Delta J_{\text{N}_2\text{O}}$ approximation also appears valid. © 1998 American Institute of Physics.

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INTRODUCTION

The discovery that resonant enhanced vibration–vibration (V–V) energy transfer is responsible for lasing action in the discharge-pumped CO_2 and CO lasers^{1–5} has provided strong motivation for its extensive study. With inverted temperature dependence (typically $\langle P_{V-V} \rangle \sim T^{-1}$), near resonant V–V energy transfer can be an important, often dominant, vibrational energy transfer pathway at low temperatures. While it is clear from a perturbation-theoretical point of view that minimizing the energy defect may enhance the energy transfer probability (if the coupling matrix element is significant), it is not clear what molecular motions can effectively compensate a finite energy defect. What allows compensation of the energy defect is the essential physical element determining the energy widths, and thereby, the overall importance of V–V energy transfer. Obtaining insight into the energy defect compensation is the subject of this paper.

The earliest attempts to understand near resonant V–V energy transfer showed that optical-like selection rules, resulting from long-range dipole–dipole or dipole–quadrupole interactions, are useful in understanding V–V exchange.^{6,7} For systems with energy defects less than 20 cm^{-1} , excellent agreement between experimental and theoretical V–V transition probabilities and temperature dependencies was found.⁸

These simple models, however, drastically underestimated the importance of V–V energy transfer for larger en-

ergy defects.⁹ A common approximation that might be blamed for this problem is the so-called straight line trajectory, i.e., translationally elastic, approximation. However, even where this approximation has been avoided a large discrepancy between theory and experiment was found.¹⁰ A mechanism based solely on long range dipole–dipole or dipole–quadrupole interactions requires small values of ΔJ even when considered in higher orders of perturbation theory. The lack of proper accounting of the role of rotational degrees of freedom is another possible reason for the failure of the models.

Indirect evidence from the temperature dependence of the V–V transition probability has been interpreted to indicate the importance of rotational motion in energy defect compensation.¹¹ This idea is reinforced by the fact that vibrationally elastic energy transfer often occurs with large cross sections and can result in the exchange of much more than one or two rotational quanta. Determining the relative importance of rotation vs translation in compensating the energy defect has remained a difficult problem in the field of molecular energy transfer and little direct experimental evidence is available.

There are a number of difficulties in designing an experiment to resolve this problem.^{12–15} How does one smoothly vary the energy defect without changing other physical variables? How does one detect the results of varying the energy defect without interfering artifacts? V–V processes necessarily involve vibrationally excited molecules both as reactants and products. This suggests the necessity of performing some sort of optical pumping experiment. Optical pumping of molecules to $v=1$ may, however, be unattractive, since one of the scattered products will populate $v=0$, where large

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thermal backgrounds can obliterate the signals of interest.

All of these problems are conveniently solved in a crossed molecular beams, stimulated emission pumping (SEP) experiment, the likes of which has been recently described.^{16,17} In this work we have performed experiments on highly vibrationally excited NO, prepared by stimulated emission pumping,¹⁸ to study near resonant V–V energy transfer to N₂O under single-collision, single-initial-quantum-state conditions. We observe a change in the rotational distribution of the vibrationally inelastic channel for scattered NO which suggests that most, if not all, of the energy defect is compensated by NO rotation. The ability of N₂O rotation to compensate the energy defect is also evident in observations of the vibrational dependent relaxation probability. These results give one of the clearest indications of how the energy defect is compensated in near resonant V–V energy transfer.

EXPERIMENT

The experimental setup has been described extensively in a recent publication¹⁷ and only a short description will be given here. Highly vibrationally excited NO is prepared using stimulated emission pumping in a molecular beam formed by expanding 3 atm neat NO through a pulsed valve (0.8 mm diam. orifice) into a vacuum chamber. The molecular beam is skimmed 2 cm below the nozzle. Approximately 4 cm further downstream NO is excited from the $J=0.5$ $v=0$ level in the electronic ground state $X^2\Pi_{1/2}$ to the $J=1.5$ rotational level in the $B^2\Pi_{1/2}(v=5)$ state [$R_{11}(0.5)$] by the frequency tripled output of a pulse-amplified single-mode ring dye laser ($\lambda=198$ nm, $\Delta\nu\sim 200$ MHz, 5 ns pulse duration, 2 mJ/pulse). Emission is stimulated from the excited NO molecules with an excimer (Lambda Physik EMG 200) pumped dye laser (Lambda Physik FL 3002) producing the $J=0.5$ (e or f parity) level of a vibrational level around $v=20$ in the electronic ground $X^2\Pi_{1/2}$. A beam with a density of $3\cdot 10^{12}$ molecules/cm³ highly vibrationally excited molecules and a quantum state purity of 95% is readily obtained. Only hyperfine and magnetic sub-levels are left unresolved.

A skimmed molecular beam of neat N₂O crosses the NO beam at an angle of 30° at a distance 6 cm from the preparation zone and 6.5 cm from the pulsed valve forming the N₂O beam. The rotational and vibrational distribution of the NO molecules scattered from N₂O is monitored at the molecular beam crossing region using laser induced fluorescence (LIF). Using a second excimer pumped dye laser, the scattered NO molecules are detected with LIF by excitation to the $B^2\Pi(v=4-6)$ state, depending on which vibrational state is probed. The fluorescence is collected by a $F/0.7$ lens system placed at right angles to both the molecular beams and the laser beam and is imaged onto a solar blind photomultiplier tube (Hamamatsu 166UH). The signal from the photomultiplier is processed by an oscilloscope (LeCroy 9430) and boxcar integrator (SRS 250) interfaced with a personal computer.

All three lasers as well as the NO molecular beam are operated at 10 Hz. The N₂O beam is delayed from its correct

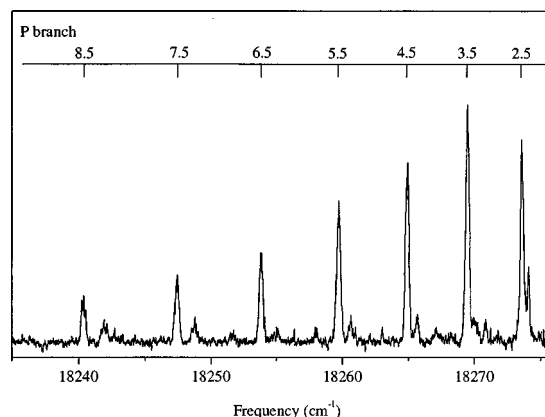


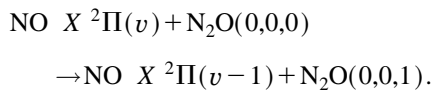
FIG. 1. Representative spectrum of the $B^2\Pi(v=5) \leftarrow X^2\Pi(v=19)$ transition after V–V energy transfer has taken place between NO $X^2\Pi(v=20 \rightarrow 19)$ and N₂O(0,0,0 \rightarrow 1). The spectrum shown is not corrected for drift in the number of prepared NO $v=20$ molecules or the laser power of the probe laser. The unassigned lines belong to the Q_{11} and R_{11} branch.

timing by 1 ms at 5 Hz (i.e., every other pulse). When delayed, collisions between the prepared NO molecules and N₂O are not possible and any apparent population transfer from the prepared state of NO results from collisions with background gas or infrared emission.^{16,19} The difference between odd and even shots is recorded using the boxcar average in “toggle mode” to distinguish the desired signal. Typically, this procedure has been repeated for 5–10 scans to yield data with an error of $\sim 15\%$.

Since the $X \rightarrow B$ transition in NO is saturated by the laser powers used in the present experiment the relative line intensities in the recorded spectra for the various rotational levels can be directly converted into relative densities once the degeneracies of the rotational levels have been taken into account. For the conversion of densities to relative cross sections it is assumed that the density to flux transformation can be neglected, which is justified in light of the arguments given in Ref. 17.

RESULTS AND DISCUSSION

In this work relative state-to-state cross sections for near resonant vibrational energy transfer between highly vibrationally excited NO and ground-state N₂O are obtained in a crossed beam setup at a collision energy of 125 ± 25 cm⁻¹. Resonant vibrational energy transfer is expected to take place via



Here (v_1, v_2, v_3) indicates the symmetric-stretch, bend, and asymmetric-stretch, respectively.

Figure 1 shows typical LIF data for inelastically scattered NO $X^2\Pi(v=19)$ observed after SEP preparation of NO $X^2\Pi(v=20)$. The relative cross sections are determined from the measured line intensities in the P_{11} branch, which is mainly composed of unblended lines. No informa-

tion on the population in the $J=1.5$ level of $v=19$ could be obtained since this state is also populated by spontaneous infrared emission from $v=20$.¹⁹

Process (1) could be observed for $v=20, 21$, and 22 , where the energy defect is $-49, -18$, and $+14$ cm^{-1} , respectively.^{20,21} Here a positive number indicates endoergicity, whereas a negative number indicates exoergicity. In addition to vibrationally inelastic channels, vibrationally elastic energy transfer was recorded for $v=22$ and 21 .

The efficiency of process (1) depends strongly on the energy defect and therefore on the prepared vibrational level of the NO molecule. Experimentally, the relative efficiency is difficult to determine precisely, but the variation with vibrational quantum number is large enough to provide clear results. Process (1) is most efficient for $v=21$ and about five times less efficient for $v=20$ and 22 . For the next lower and higher vibrational states ($v=19$ and 23), which have energy defects of -80 and $+47$ cm^{-1} , respectively, no evidence of vibrational energy transfer could be detected. This observed resonance for energy transfer for $v=21$ is clear evidence that we are indeed observing process (1), despite the fact that none of our measurements directly probe the N_2O molecule.

Remarkably, transfer from $22 \rightarrow 21$ ($\Delta E = +14$ cm^{-1}) is substantially less efficient (by about a factor of 5) than that from $21 \rightarrow 20$ ($\Delta E = -18$ cm^{-1}), despite the collision energy of 125 cm^{-1} . This is clear evidence that translational energy is ineffective in compensating the positive energy defect for the $22 \rightarrow 21$ channel. In contrast, if N_2O rotation were fully effective in compensating the energy defect, the molecular beam sample could have only $\sim 1/5$ of its population at total rotational energies greater than 14 cm^{-1} . (Recall that NO is prepared in $J=0.5$, so only N_2O rotation and relative translation are available to compensate the positive energy defect.) The rotational temperature required to fulfill this expectation is 10 K, a temperature quite consistent with typical molecular beam conditions. At this temperature less than 1% of the N_2O sample has a total rotational energy greater than 47 cm^{-1} (energy defect for the $23 \rightarrow 22$ channel). These relative vibrational intensities are clear yet indirect evidence suggesting rotational motion is more important in energy defect compensation than translation.

The role of NO becomes clear when looking at its rotational energy distributions for vibrationally elastic and inelastic channels. These are shown in Fig. 2. The upper panel shows the relative state-to-state cross sections for spin-orbit conserving ($^2\Pi_{1/2} \rightarrow ^2\Pi_{1/2}$) vibrationally elastic transfer of NO $X^2\Pi_{1/2}$ $J=0.5$ with N_2O for $v=20$ and 21 (peak normalized). It is clear that the rotational energy transfer is quite similar for both vibrational levels. In previous work (rotational energy transfer of NO with He) it was found that the vibrational influence on the rotational energy transfer could be largely accounted for by a rigid rotor three-particle scattering calculation where the NO bond length was fixed at the vibrationally averaged value.¹⁷ Since the vibrationally averaged bond length for $v=20$ and 21 are nearly identical, the present result is not surprising.

In comparison, the lower panel of Fig. 2 shows the relative state-to-state cross sections for vibrationally inelastic channels ($^2\Pi_{1/2} \rightarrow ^2\Pi_{1/2}$). Spin-orbit changing transitions

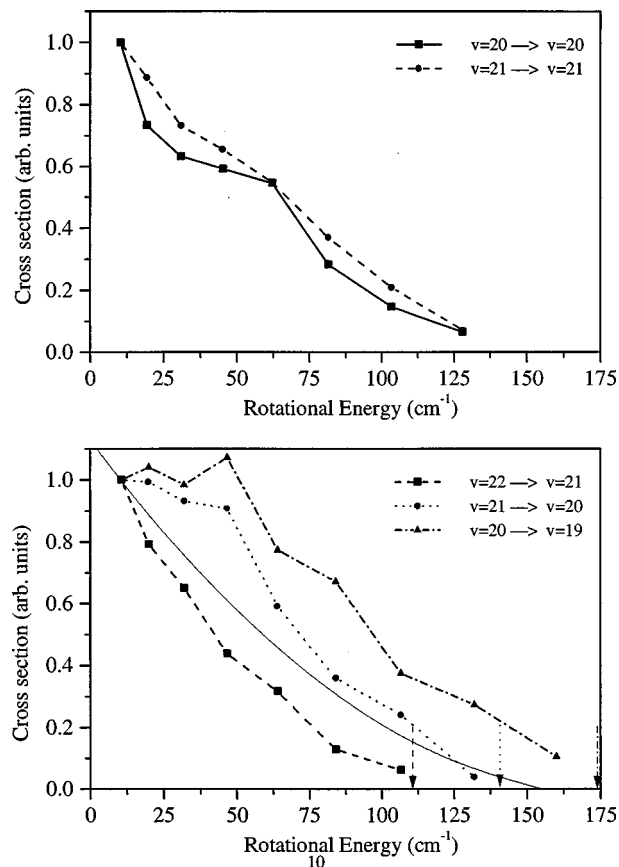


FIG. 2. Upper panel (vibrationally elastic channels): Relative state-to-state cross sections for NO $X^2\Pi_{1/2}(v, J=0.5 \rightarrow J')$ for Ω conserving collisions with N_2O (collision energy: 125 cm^{-1}). Lower panel (vibrationally inelastic channels): Same as upper panel but for near resonant V-V channels, i.e., NO $X^2\Pi_{1/2}(v \rightarrow v-1, J=0.5 \rightarrow J')$. The solid line is a quadratic fit to the average of the data of the upper panel. This shows the degree of rotational excitation expected from the angular anisotropy of the interaction potential. The vibrationally inelastic channels are shifted with respect to the solid line approximately by their V-V transfer energy defect. Energetic limits are shown as arrows.

($^2\Pi_{1/2} \rightarrow ^2\Pi_{3/2}$) could not be observed in the vibrationally inelastic channels, although they are energetically accessible for the $v=20$ and 21 .²⁰ The distributions are (peak) normalized to show differences in their shapes. For comparison, the solid line shown in the figure is the result of a quadratic fit to the average of the vibrationally elastic data of the upper panel. This allows one to see the degree of rotational excitation that occurs purely due to the angular anisotropy of the interaction potential unrelated to the V-V transfer.

The rotational distributions for the vibrationally inelastic channels are clearly shifted with respect to the solid line. The endoergic channel ($22 \rightarrow 21$) is rotationally cooled (shifted to lower energies by ~ 18 cm^{-1}). The two exoergic channels are rotationally hotter (shifted to higher energies by ~ 14 and 49 cm^{-1} , respectively). This plot clearly shows that the smooth variation of the energy defect with vibrational quantum number is (nearly completely) compensated for by NO rotational energy.

The twin conclusions: (1) N_2O rotation promotes the endoergic ($22 \rightarrow 21$) process and (2) NO rotational distributions are shifted approximately by the value of the vibrational state specific energy defect, are consistent if $\Delta J_{\text{NO}} \geq \Delta J_{\text{N}_2\text{O}}$. The

equal sign obtains for any dynamical model where the orbital angular momentum is conserved by the collision (for example, the straight line trajectory model). N_2O 's rotation constant ($B_0 = 0.4182 \text{ cm}^{-1}$) is substantially smaller than that of NO ($B = 1.309 \text{ cm}^{-1}$ for $v = 21$), meaning that about three times more energy is accepted by NO in comparison to N_2O if $\Delta J_{\text{NO}} = \Delta J_{\text{N}_2\text{O}}$.

In light of these results and those presented above, it now appears clear that models of near resonant V–V energy transfer are likely to fail (in predictions of the energy widths) unless they adequately account for the role of rotational excitation. It would appear that an explicit treatment of translational inelasticity may, however, be less important. Similar experiments on other collision systems would be helpful in establishing the generality of this conclusion.

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